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OVERVIEW

Mechanical Properties and Microstructure of Magnesium-Aluminum Based Alloys Containing Strontium

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The mechanical properties and processing performances of conventional magnesium alloys still could not meet the need of important application fields due to some demerits, such as poor formability, low creep resistance and unsatisfactory strength at elevated temperature. Recent investigations have shown that additions of strontium to magnesium alloys are effective in improving creep resistance of the alloys at temperatures above 150°C, and some new types of magnesium alloys containing strontium have been developed. The mechanical properties and microstructure of magnesium-aluminum based alloys containing strontium are reviewed, and the considerable discrepancy among the research results is discussed. Special attentions are paid to the mechanical properties, compounds and grain refinement of Mg-Al-Sr based alloys. The Sr/Al ratio is thought to be important to control the microstructure of Mg-Al-Sr alloys. The mechanism of grain refinement caused by strontium addition in magnesium alloys remains unclear. [doi:10.2320/matertrans.MOV2007315]

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1. Introduction

Magnesium alloys have attracted an increasing interest in transportation, aeronautical and aerospace industries in the past decade because of their low density, but their mechanical properties and processing performances still could not meet the need of some important parts in vehicles and in other important application fields due to their poor formability and restricted creep properties.[1–4] Therefore, a lot of ways are being investigated in the world in order to further improve the mechanical properties and processing performances of the magnesium alloys.[5–16] Alloying is an important method used by many researchers. In recent years, Mg–Al–Sr alloy system has emerged as potential heat-resistant Mg-alloys. The formation of compounds containing Sr was thought to be very beneficial for improving the elevated temperature properties. Besides, strontium was found to be a potential effective grain refiner for magnesium alloys.[2] In the present paper, the composition design of new type magnesium alloys containing Sr is introduced, and the effects of Sr addition on the microstructure and properties of magnesium alloys are reviewed and discussed.

2. Mechanical Properties of New Type Magnesium Alloys Containing Strontium

When strontium is used as a main element in magnesium alloys, the addition of Sr is to improve mainly the elevated temperature properties, especially creep resistance, by the formation of the heat-stable alloy compounds containing Sr. AJ alloy (Mg-Al-Sr alloy) is a representative alloy series in the heat-resistant magnesium alloys containing Sr. In the past decade, new types of Mg-Al-Sr-based alloys like AJ50X, AJ52X and AJ62X have been successfully developed by adding various amount of Sr to the AM50 commercial magnesium alloy by Noranda Inc. (Table 1).[5–9] The Mg-Al-Sr-based alloys (AJ alloys) are found to have superior creep performance and tensile strength at temperatures as high as 175°C. Among these alloys, Mg-6Al-2.4Sr (AJ62X) exhibits an optimum combination of creep resistance and excellent castability, and AJ62LX has better ductility than other AJ alloys. Yusuke *et al.* found that Ca addition of more than 1 mass% to AM50 alloy not only significantly improved creep resistance but also enhanced casting crack tendency.[10] By the addition of about 0.2 mass% Sr, the casting cracks could be suppressed significantly. Besides, the creep resistance of the alloys increased.

Table 1 The Compositions of new type Mg-Al-Sr based alloys.[5–12]

Alloys	Composition, wt%				
	Al	Sr	Mn	Ca	Mg
AJ50X	5	0.5	0.2–0.3	—	Bal.
AJ52X	5	2.0	0.2–0.3	—	Bal.
AJ62X	6	2.4	0.2–0.3	—	Bal.
AJ62LX	6	<2.1	0.2–0.3	—	Bal.
AJC411	3.8–4.2	0.8–1.2	0.3–0.5	0.8–1.2	Bal.
AJ42	4	2	0.3	—	Bal.
AJC421	4	2	0.3	1	Bal.
AJC511	4.8–5.2	0.8–1.2	0.3–0.5	0.8–1.2	Bal.
AJC611	5.8–6.2	0.8–1.2	0.3–0.5	0.8–1.2	Bal.
AJC711	6.8–7.2	0.8–1.2	0.3–0.5	0.8–1.2	Bal.

Bai Jing and co-wokers also tried to develop several kinds of Mg-Al-Sr alloys, namely AJC411, AJC511, AJC611 and AJC711 by adjusting the contents of Al and Ca (Table 1). The research results obtained by Bai *et al.*[11] revealed that the AJC611 alloy showed the best creep resistance at 175°C and AJC511 alloy showed the best creep resistance at 200°C among tested alloys (Fig. 1). In addition, Bai *et al.*[12] investigated the effect of extrusion process on microstructures and mechanical properties of Mg-4Al-2Sr (AJ42) and Mg-4Al-2Sr-1Ca (AJC421) alloys, and found that the creep

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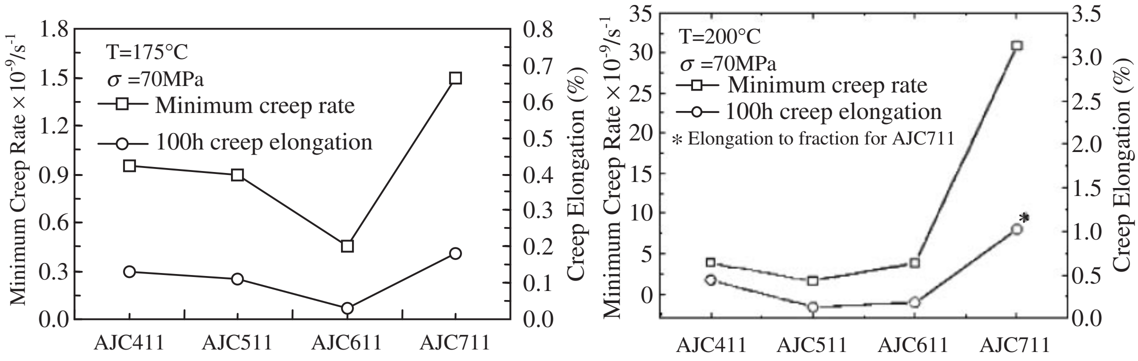

Fig. 1 Minimum creep rate and 100 h creep elongation for AJC411-711 alloys.[11,12)]

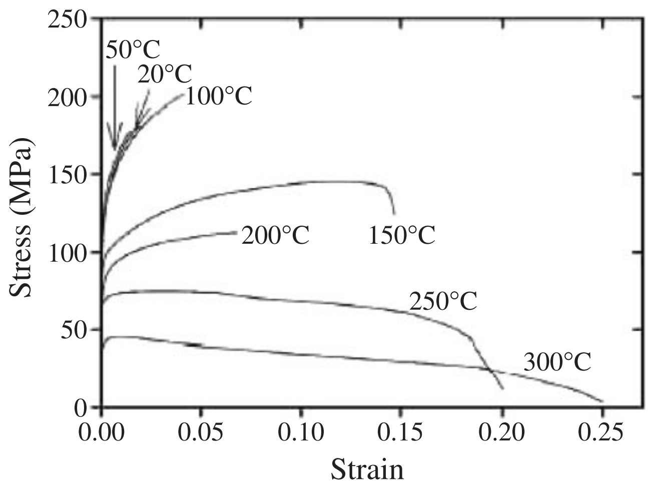

Fig. 2 Stress-strain curves of AJ50 alloy at various temperatures.[13)]

temperature and 150°C (Fig. 3).[14)] The results showed that trace addition of strontium to the alloy had a positive effect on the mechanical properties of the Mg–5Al alloy, especially on ultimate tensile strength and elongation. The mechanical properties increased with increasing strontium content when the strontium addition was lower than 0.1 mass%. However, greater amount of strontium decreased the ultimate tensile strength and elongation of the AM50 alloy whereas increased the yield strength at room temperature. Tensile strength of the Mg–5Al–0.1Sr alloy was 27% better than that of the Mg–5Al–1Sr alloy at room temperature. Figure 3(b) shows the tensile properties of the alloys tested at 150°C. Strontium greatly improved the high temperature tensile strength and elongation. Trace addition of strontium, similar to the results at room temperature, had a positive effect on mechanical properties of the Mg–5Al alloy at elevated temperature. However, 1 mass% addition of strontium also improved the tensile properties at elevated temperature, which was different from the results at room temperature.

resistances of both alloys were obviously reduced after extrusion deformation. Zuzanka *et al.*[13)] investigated the deformation behavior of the ternary magnesium alloy, Mg-5Al-0.6Sr (AJ50), in uniaxial tension tests at temperatures between 20°C and 300°C and at an initial strain rate ranging in the order of $10^{-5}\,s^{-1}$, and found that the yield stress as well as the maximum stress of the alloy were very sensitive to the testing temperature (Fig. 2).

Zhao and co-workers investigated the effects of the Sr content on the tensile properties of Mg-Al-Sr alloys at room

Several typical creep strain curves and the steady creep rate curve obtained from the constant load and constant temperature test (175°C/70 MPa) for the Mg–5Al–xSr alloys are shown in Fig. 4.[14)] Although trace strontium addition increased the primary creep strain of the Mg–5Al alloy, the minimum creep rate decreased with the increase of strontium content. Creep curves of the AM50 alloy presented a very short secondary creep stage. Creep life of the AM50 alloy was only about 64 h, and creep rate is as high as $4.04 \times 10^{-7}\,s^{-1}$. With the strontium addition of 0.02 mass%, the

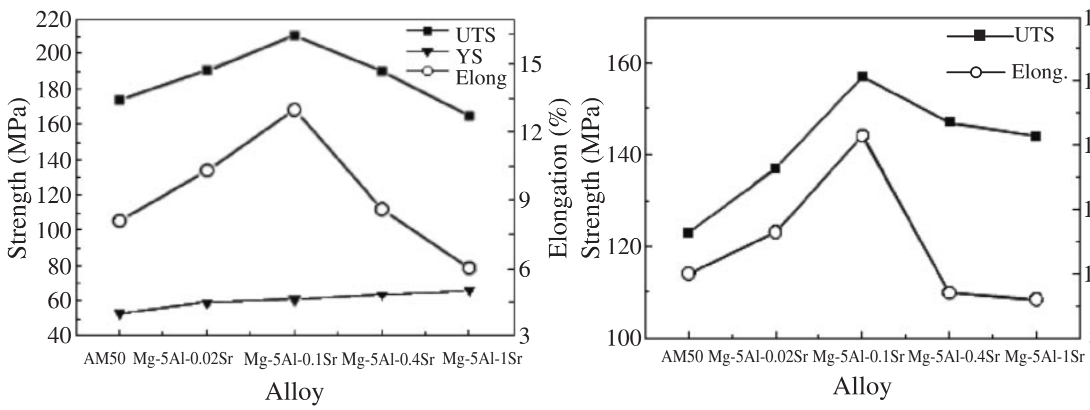

Fig. 3 Tensile properties of the Mg–5Al–xSr alloys at room temperature (a) and 150°C (b).[14)]

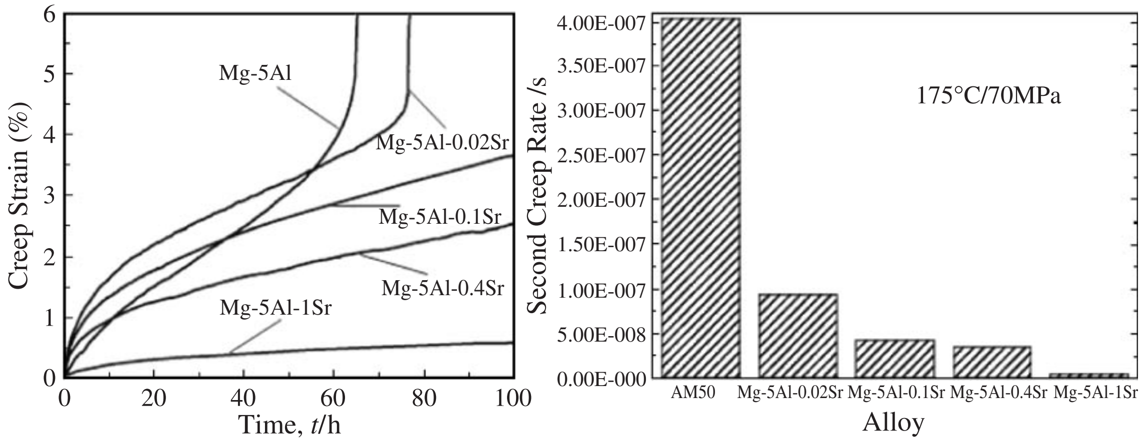

Fig. 4 Creep properties of as-cast Mg–5Al–*x*Sr alloy.[14] (a) the creep curve; (b) the second creep rate.

creep rate of as-cast alloy reduced to $9.41 \times 10^{-8}\,s^{-1}$ and the creep life increased to 80 h. Further improvement of creep resistance was achieved when 0.1 mass% strontium was added to the alloy. The lowest creep rate obtained from the Mg–5Al–1Sr alloy was $5.1 \times 10^{-9}\,s^{-1}$, two orders of magnitude lower than that of the base alloy (AM50). Dargusch and co-workers investigated the microstructure and mechanical properties of high pressure die cast magnesium alloy AE42 with 1 mass% strontium.[15] The addition of 1 mass% Sr to AE42 was found to results in an improvement in the tensile strength of the alloy at elevated temperatures of 150°C and 175°C and an improvement in the constant load creep properties at 175°C.

The improvement of mechanical properties of magnesium alloys at elevated temperature by the addition of strontium could be mainly attributed to the suppression of grain boundary sliding due to the creation of thermally stable compounds containing strontium along the grain boundaries and the suppression of discontinuous precipitation of β-$Mg_{17}Al_{12}$ phase.[10] The alloying elements in solution were thought to lead to formation of planar defects spreading on the basal plane of the magnesium matrix, which acted as obstacles to non-basal slip of dislocations. However, the effect of strontium on planar defects in magnesium matrix remains unclear. The improvement of the elongation at room temperature could be mainly attributed to the refinement of grains by the addition of strontium, but the increase in the volume fraction of compounds containing strontium was thought to have a negative effect on the elongation of alloys.

3. Microstructure of New Type Magnesium Alloys Containing Strontium

Effects of strontium on the microstructure of magnesium alloys are found to be very apparent. In the past decade, more attentions were paid to the change of compounds and grain refinement in the Mg-Al-Sr alloys. In many cases, the effects of strontium on the microstructure depend on the content of aluminum and calcium. The formation of new compounds was thought to be a main factor that improves the elevated temperature properties.

The early work on the phases of Mg–Al–Sr system was carried out by Makhmudov and co-workers in 1980s. However, there is obvious inconsistency between their works. Baril *et al.*[6] investigated four samples in the Mg-rich region of the Mg–Al–Sr system and tentatively designated a ternary phase as $Al_3Mg_{13}Sr$. In their work, the stoichiometry is not clearly identified and the chemical composition is not compatible with the ternary compound $Al_{34}Mg_6Sr_{60}$ reported in early work. Czerwinski and Zielinska-Lipiec[13] investigated the microstructural evolution of a Mg-5Al-2Sr alloy and reported the common feature that the Sr-containing phases in the as-cast ingots was at grain or sub-grain boundaries. The presence of $Mg_{17}Al_{12}$ suggests that there is an insufficient amount of Sr to bind all the aluminum atoms. At the same time, however, Sr reacted exclusively with Mg to form $Mg_{17}Sr_2$. Hence, it is very likely that the local segregation of Al and Sr led to a variety of phases. The microstructure of AJ alloys was found to be characterized by a lamellar Al_4Sr-α(Mg) phase that formed at the interdendritic/grain boundary region of the primary magnesium matrix.[5–9] Mg-5Al-2Sr (AJ52X) had a ternary phase that was tentatively named as $Al_3Mg_{13}Sr$. When the strontium level was low in AJ62X, the volume fraction of Al_4Sr was reduced. As a result, the supersaturation of aluminum in the primary magnesium phase increased, and $Mg_{17}Al_{12}$ formed.

Bai Jing *et al.*[11] recently investigated the microstructure of Mg–Al–Sr (AJ) based alloys and reported that a ternary phase existed in the alloys containing 2–3 mass% Sr at the grain boundaries. In the Mg-5Al alloy with addition of 1.2 mass% Sr, A1-Sr eutectic and divorced Mg-Sr-A1 phases would form. When the addition of 1.8 mass% Sr was used, the lamellar Mg-A1-Sr eutectic formed instead. The compounds containing Sr were found to distribute along grain boundaries and were more heat-stable than $Mg_{17}A1_{12}$. With the appearance of Sr-containing phases and decrease of the amount of less heat-stable $Mg_{17}A1_{12}$, better creep resistance of the alloy could then be obtained. It was found that after hot extrusion, the intermetallics in the AJ42 and AJ421 alloys were converted into band structure, and eutectic phases were crushed into small blocks.

The microstructure of the AJC411-711 alloys was also investigated by Bai Jing *et al.*[12] The research results indicated that thin lamellar eutectic Mg_2Ca, coarse eutectic

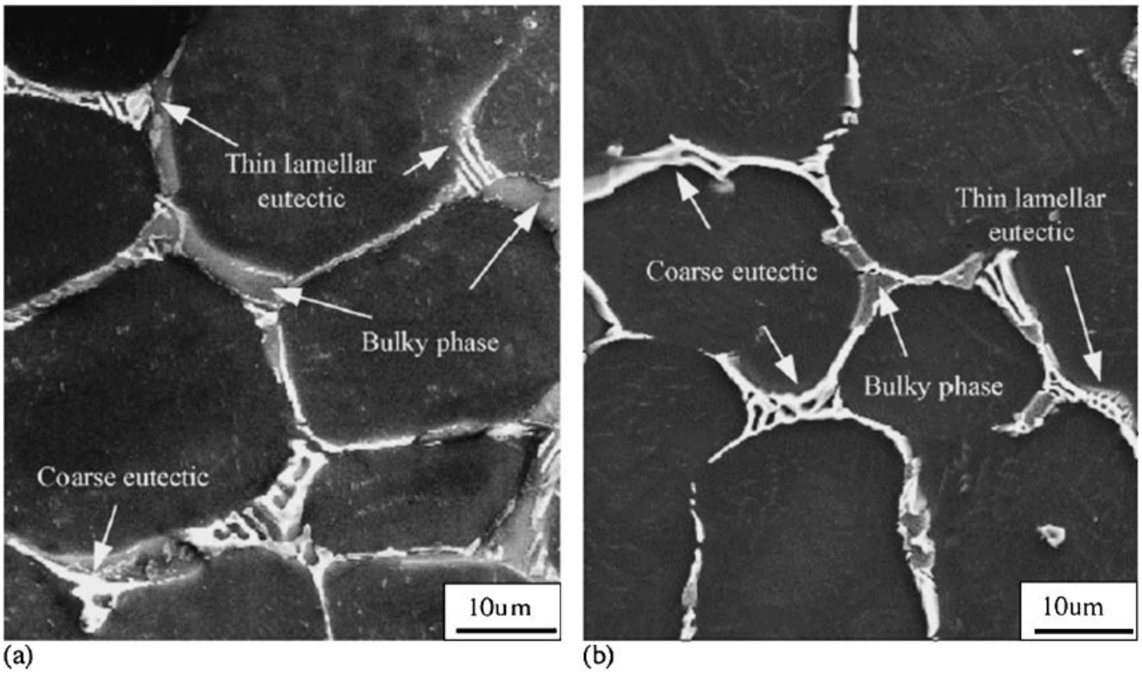

Fig. 5 SEM photos of the as-cast alloys. (a) AJC411; (b) AJC511.[12)]

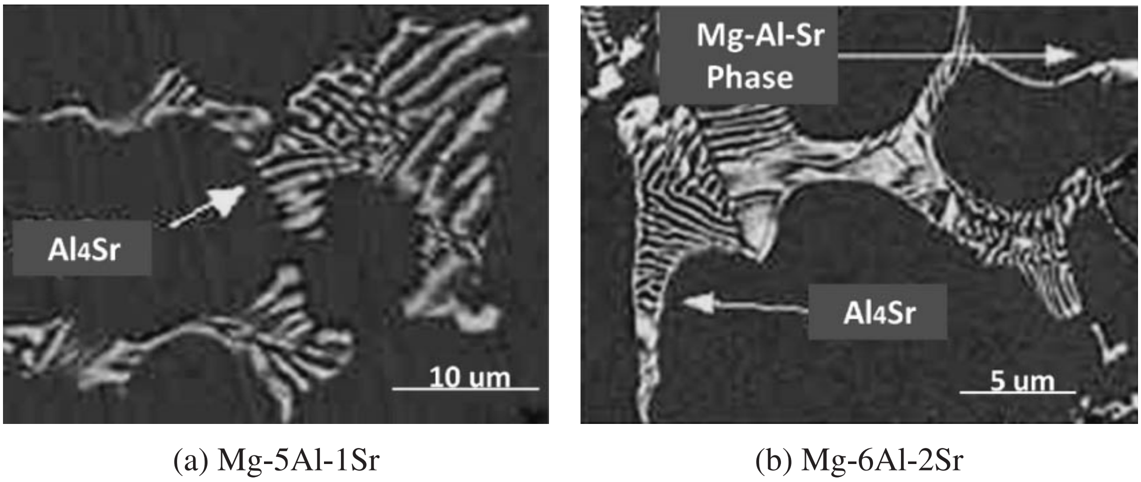

Fig. 6 Microstructure of die casting Mg-Al-Sr alloys.

$(Mg,Al)_2Ca$ and a bulky ternary Mg-Al-Sr phase in the AJC411 alloy were observed at grain boundaries (Fig. 5). With an increase of Al content, the volume fraction of the Mg_2Ca and Mg-Al-Sr phase decreased, while that of the coarse $(Mg,Al)_2Ca$ phase increased. Aluminum addition of 7 mass% led to the formation of another thin lamellar eutectic Al_4Sr at grain boundaries instead of the eutectic $(Mg,Al)_2Ca$.

In ternary Mg–Al–Sr alloys, three types of compounds containing Sr had been reported,[23)] Al_4Sr, $Mg_{17}Sr_2$ and $Mg_{38}Sr_9$. Magnesium was found to dissolve in Al_4Sr, which could be represented by $Mg_xAl_{4-x}Sr$. This compound had plate-like structure. The maximum solubility of Al in $Mg_{17}Sr_2$ in the test samples was found to be 21.3 atom%. It was also observed that $Mg_{38}Sr_9$ dissolved 12.5 aomt% Al. A very negligible solubility of Sr in β-$Mg_{17}Al_{12}$ and γ-Al_3Mg_2 was detected by EPMA analysis. The extended solid solubility of the binary compounds agrees with the experimental isothermal section of the Mg–Al–Sr system at 300 K. This isothermal section shows a triangulation involving $Mg_{17}Sr_2$, Al_4Sr and Mg_2Sr.

The Sr/Al ratio is thought to be important to control the microstructure of Mg-Al-Sr alloys. Pekguleryuz[8,9)] reported that Mg-Al-Sr based alloys showed different microstructures with the change of Sr/Al ratio. When the Sr/Al ratio was below 0.3, the Al_4Sr and/or $Mg_{17}A1_{12}$ phases were found in the microstructure (Fig. 6(a)). When the Sr/Al ratio was higher, a new ternary Mg-Al-Sr compound was observed (Fig. 6(b)). When the Sr/Al ratio was very low, there was an insufficient amount of Sr to bind all the Al atoms and the excess Al would form the $Mg_{17}Al_{12}$ phase. These results were confirmed by Parvez *et al.*[7)] who investigated 22 alloys in the Mg-Al-Sr system. They found that Al_4Sr and α-Mg were the dominating phases. Besides, they also found a new $Al_3Mg_{13}Sr$ phase.

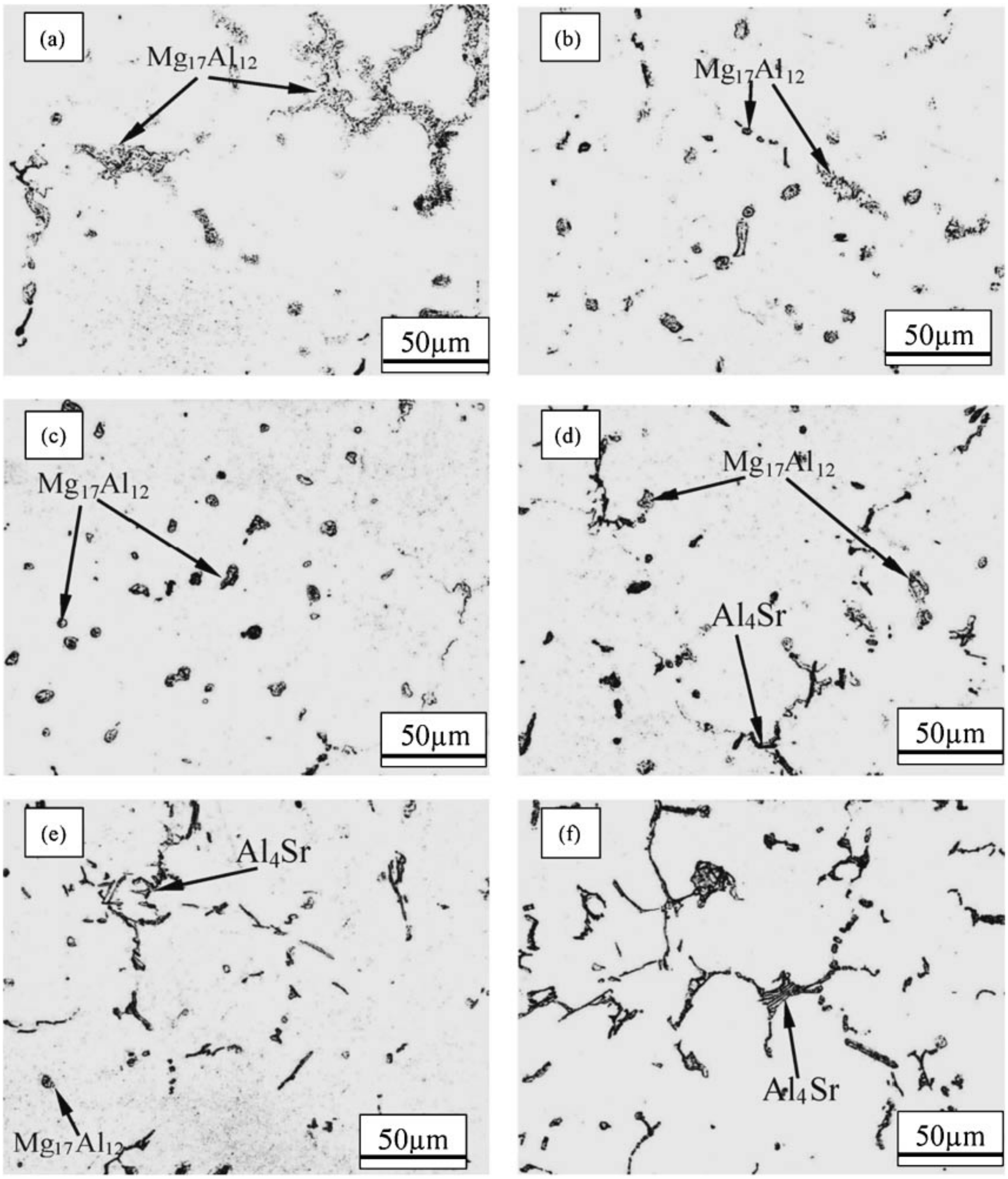

Fig. 7 Microstructure of as-cast Mg–5Al–*x*Sr alloy:[14] (a) Mg–5Al; (b) Mg–5Al–0.02Sr; (c) Mg–5Al–0.1Sr; (d) Mg–5Al–0.4Sr; (e) Mg–5Al–0.7Sr; (f) Mg–5Al–1Sr.

Figure 7 shows the optical micrographs of the as-cast microstructure of Mg–5Al–*x*Sr alloys.[14] The microstructure of Mg–5Al consisted of primary Mg, coarse divorced $Mg_{17}Al_{12}$ particles and discontinuous $Mg_{17}Al_{12}$ precipitates, all at the grain boundaries. Trace addition of strontium refined the as-cast microstructure, especially the second phases. The Coarse divorced eutectic phase turned into fine spherical particles and its distribution was more uniform than in Mg–5Al alloy. The spherical phase in the Mg–5Al–0.1Sr alloy contained small particles inside, acting as nucleation sites for $Mg_{17}Al_{12}$ phase (Fig. 7(a)). The nucleus of $Mg_{17}Al_{12}$ phase contained significant amount of strontium, which indicated strontium mainly dissolved into particles. When strontium content was more than 0.4 mass%, a lamellar intermetallic phase, Al_4Sr, was observed and the volume fraction of particles decreased. Higher strontium addition caused further reduction of the volume fraction of particles, and few particles existed in the Mg–5Al–1Sr alloy because of the formation of Al_4Sr phase. The amount of Al_4Sr phase increased with an increasing strontium content. For Mg–5Al–1Sr alloys, lamellar Al_4Sr phase distributed like a network can be clearly seen at the grain boundaries Fig. 7(d)–(f).

Zhao *et al.*[14] investigated the microstructure of Mg–5Al based alloys with Sr and Ti additions. Their research results indicated that small addition of Sr mainly dissolved into $Mg_{17}Al_{12}$ particles and increased their thermal stability and creep strength. Sr addition of higher than 0.4 mass% could result in the formation of Al_4Sr phase, which suppressed the formation of $Mg_{17}Al_{12}$ phases. The authors' recent results revealed that addition of 0.06 mass% Sr to Mg-6Al-1Zn-0.7Si magnesium alloy could result in transformation of the morphology of Mg_2Si phases from the coarse Chinese script shape to small block shapes. Similar result was obtained by Yuan *et al.*[17] In addition, Nam *et al.*[18] also found that the modification efficiency of Sr to Mg_2Si phase in the microstructure of containing-Si magnesium alloys was better than that of Sb element. The effect of strontium on the microstructure of AZ31 magnesium alloy was investigated by Zeng *et al.*[19] Three types of phases, blocky-shaped $Mg_{17}Al_{12}$ acicular $Mg_{20}Al_{20}Mn_5Sr$, and insular $Mg_{16}(Al,Zn)_2Sr$, were identified in the Sr-containing AZ31 alloys. With an increasing cooling rate, the volume fraction of blocky-shaped $Mg_{17}Al_{12}$ phase increased, and the volume fraction of acicular $Mg_{20}Al_{20}Mn_5Sr$ phase diminished. Besides, the insular $Mg_{16}(Al,Zn)_2Sr$ phase was refined and granulated.

The phase diagrams of Sr-containing magnesium alloys are important base for investigation on the compounds of Mg-Sr based alloys. However, only limited work has been done on the phase diagrams of magnesium alloys containing Sr.[7,20,21] In 2003, Koray *et al.*[20] calculated the liquidus projection of the ternary Mg–Al–Sr system, and the calculated phase diagram exhibited substantial disagreement with the experimental data. The extended solubility between the solid phases was not considered in the thermodynamic assessment. In 2004, Liu *et al.*[15] reported the potential existence of Al_3Sr_8 and Al_5Sr_4 compounds. In 2005, the investigation on the phase diagram of the ternary Mg–Al–Sr system was completed with 22 different alloys by Parvez and co-workers,[7] and liquidus temperature and enthalpy were determined. Al_4Sr and α-Mg were found to be the dominating phases in the investigated alloys. Four new phase fields had been identified. The new phases were tentatively designated as $\tau 1$, $\tau 2$, $\tau 3$ and $\tau 4$, which may be ternary intermetallics or solid solutions. Some peak positions of $\tau 1$ corresponded well with the newly reported ternary compound $Al_3Mg_{13}Sr$. The structure and composition of $\tau 2$, $\tau 3$ and $\tau 4$ remained unknown. The identified phases in the as-cast condition were found consistent and thermodynamically stable with the post-DSC sample (25°C ↔ 700°C) in the investigated alloys. Two ternary eutectic transformations had been observed. A considerable discrepancy in the solid-phase transformation temperature was observed. Predicted phases by the thermodynamic calculation did not agree with the XRD results in nine samples, which suggested that this system should be remodeled. Figure 8 is one of phase relationship diagrams obtained.

The effects of strontium on the grain size of magnesium and its alloys were found to be also obvious,[22–33] which could be used to improve the plasticity and formability of magnesium alloys, although little work has been carried out on effects of strontium on the plasticity and formability. The research results obtained by Lee *et al.*[22] showed that the grain size of magnesium and its alloys with low Al content could be reduced by adding minor Sr, but the refinement efficiency for magnesium alloys with high Al content was not obvious. In addition, Zeng *et al.*[19] reported that the refinement efficiency of Sr to AZ31 magnesium alloy was affected by cooling rate. For a given Sr addition, the grain size of AZ31 alloy decreased with the increase of cooing rate (Fig. 9). Kinji Hirai *et al.*[31] investigated the effects of Ca and Sr additions on the microstructure of a cast AZ91 magnesium alloy, and found that the grain size was decreased to about 40 µm with adding the Sr element to AZ91. It was noted that the grain size in AZ91 + Ca + Sr alloy is finer than that in AZ91 + Sr alloy, and the grain size with adding 0.5 mass% Sr and 1.0 mass% Ca was further refined to be about 17 µm. More recently, the effect of strontium addition and electromagnetic stirring on the microstructure of AZ91 alloy was investigated by Liu *et al.*[32] It was found that Sr addition ranging from 0.1 to 0.3 mass% caused refinement of the as-cast microstructure, but did not form any new phases. Combination of strontium addition and electromagnetic stirring not only significantly decreased the grain size but also reduced the volume percentage of $Mg_{17}Al_{12}$ phases.

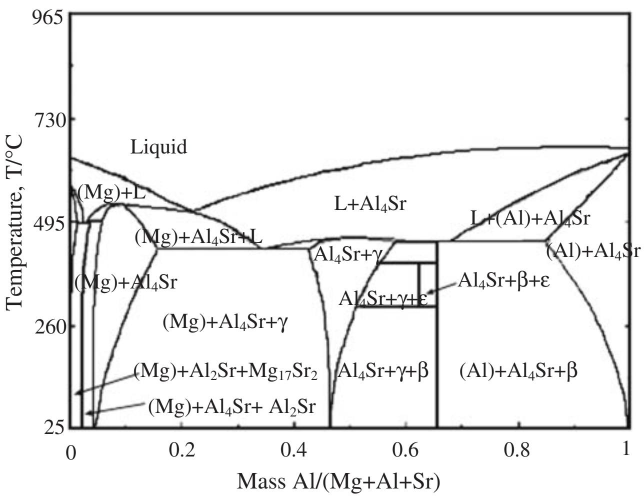

Fig. 8 The calculated vertical section at constant 3.32 mass% Sr with DSC signals.[7]

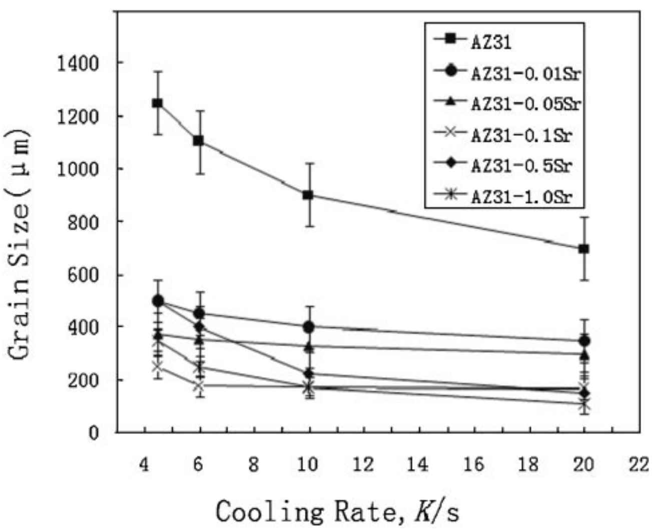

Fig. 9 Effects of cooling rate on the grain size of AZ31 + xSr alloys.[19]

The authors' recent work paid more attention to effects of the types and states of master alloys containing Sr on the grain refinement of magnesium alloys.[2,31] The experimental results revealed that Al-Sr and Mg-Sr master alloys with

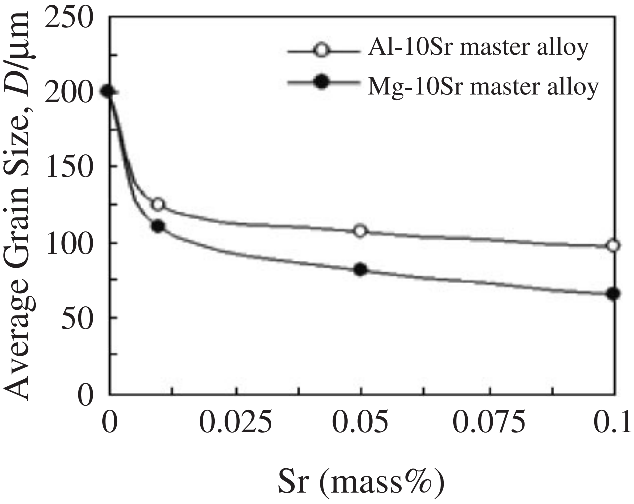

Fig. 10 Effect of Sr addition on grain size of AZ31 alloy.[2)]

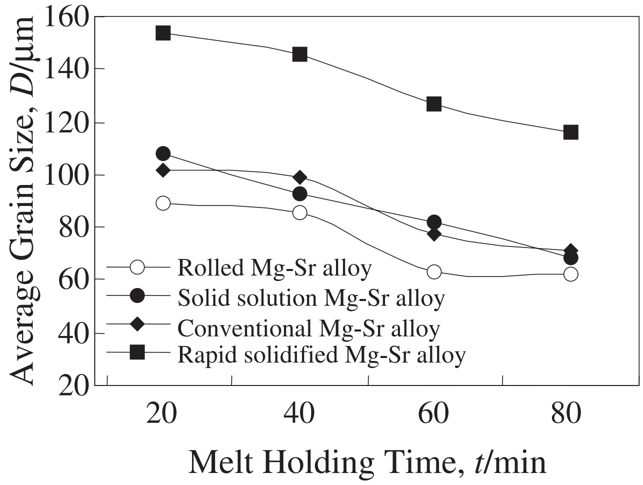

Fig. 11 Effects of Mg-Sr master alloys with different states on the grain size of AZ31 alloy.[2)]

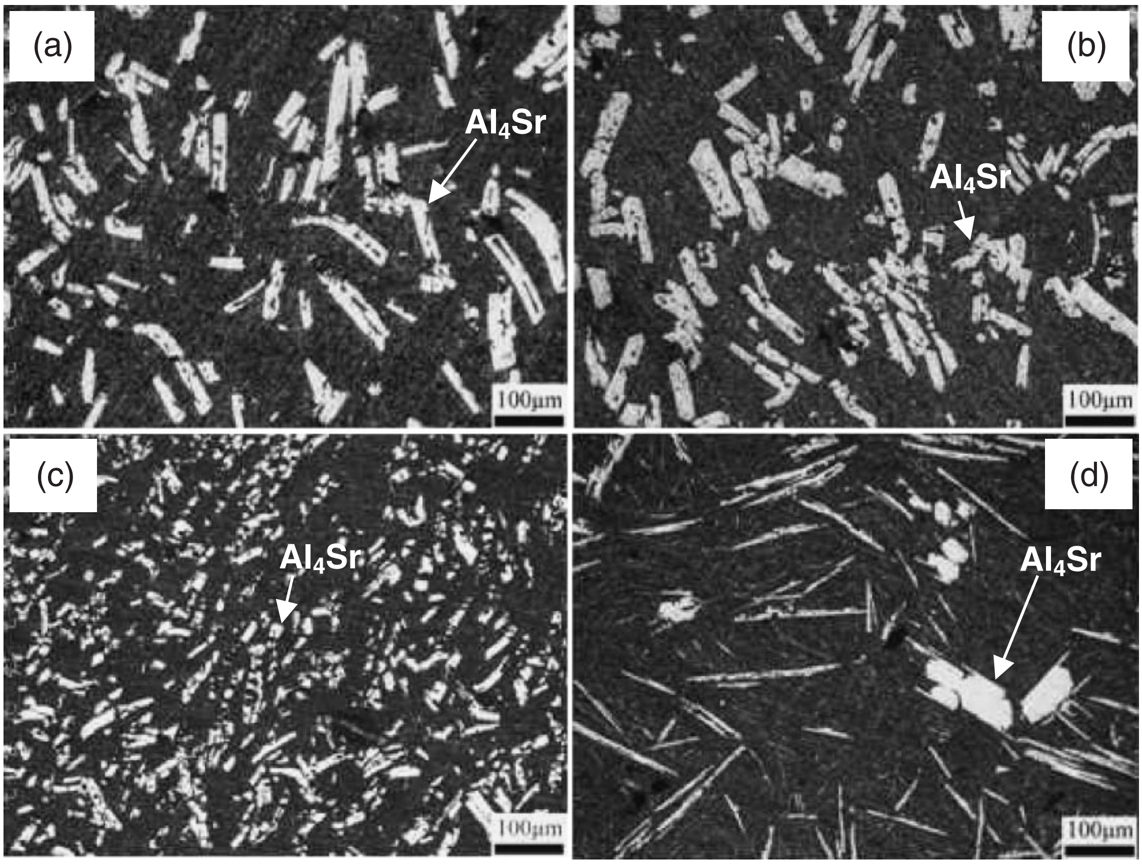

Fig. 12 Microstructures of Al-10Sr master alloys. (a) as-received; (b) after solution; (c) as-rolled; (d) as-RS (by rapid solidification).

different states had different effects on the grain refinement of magnesium alloys (Fig. 10). The refinement efficiency of Mg-10Sr master alloy to AZ31 alloy was found to be higher than that of the Al-10Sr master alloy (Fig. 10). Although the refinement of Al-10Sr alloy on the grain is not such apparent as Mg-10Sr alloy, the Al-10Sr alloy is a potential refiner due to its low cost. The states of master alloys were found to be also important to obtain ideal refinement efficiency. For the Al-10Sr master alloys, the refinement efficiency of as-rolled, as-remelt master alloys and the master alloy prepared by rapid solidification process was higher than that of conventional Al-10Sr master alloys. However, the refinement efficiency of the Mg-10Sr master alloy prepared by rapid solidification process was lower than that of as-received and as-rolled Mg-10Sr master alloys (Fig. 11). The difference of refinement efficiency possibly related to change of the morphology and distribution of the second phases in the microstructures of master alloys (Fig. 12 and Fig. 13).

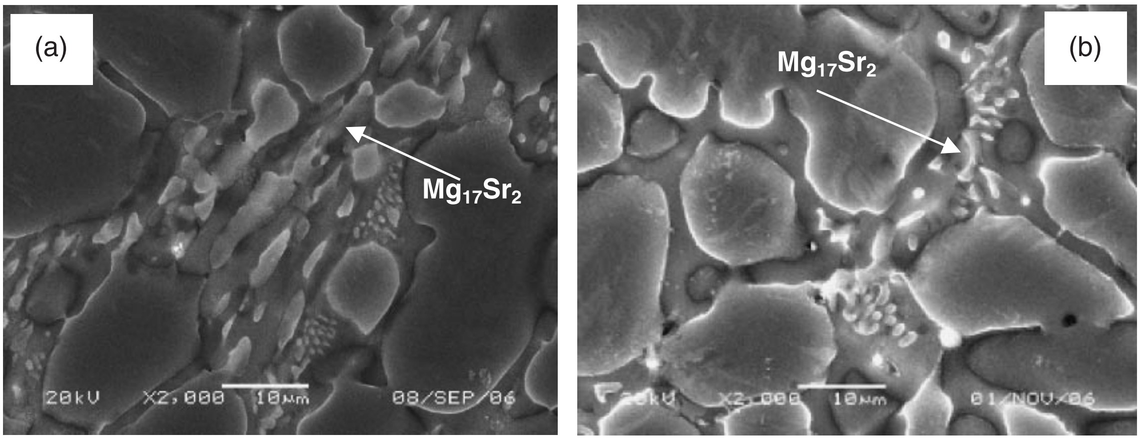

Fig. 13 The Microstructures of Mg-10Sr master alloys with different states (a) As-received; (b) as-rolled.

So far, the mechanism of grain refinement caused by strontium addition remains unclear. Based on the classic solidification theory, grain size depends mainly on three factors: the effective number of potential crystal nucleus in the melt, nucleation ratio and growth rate. Because the $Mg_{17}Sr_2$ phase has big mismatch degree with magnesium, it is not possible that the $Mg_{17}Sr_2$ phase works as nucleus of new phase during solidification. The segregation of strontium in the solid/liquid interface might be a main factor, which could inhibit the growth of as-cast grains during solidification.

4. Summary

Strontium is used in magnesium alloys mainly for refining as-cast grain as well as improving mechanical properties at elevated temperature. Mg-Al-Sr-based alloys (AJ alloys) were found to have superior creep performance and tensile strength at temperatures as high as 175°C. The Mg-6Al-2.4Sr (AJ62X) alloy was found to exhibit a good combination of creep resistance and excellent castability, and AJ62LX had better ductility than other AJ alloys. Addition of Ca could improve further the properties of Mg-Al-Sr alloys. In the past decade, more attentions were paid to investigate the change of compounds and grain refinement in the Mg-Al-Sr alloys with the change of Sr content, and a lot of research results have been obtained. However, some research results on the phase equilibria of the Mg–Al–Sr system are self-contradictory. It is very important to make a detailed and complete study of the phase diagrams of Mg–Al(Zn)-Sr based alloys in the future. The Sr/Al ratio is thought to be important to control the microstructure of Mg-Al-Sr alloys. The effects of strontium on the grain size of magnesium and its alloys are found to be very obvious, which could be used to improve the plasticity and formability of magnesium alloys, although little work has been carried out on effects of strontium on the plasticity and formability. The mechanism of grain refinement caused by strontium addition in magnesium alloys remains unclear. The relationship between the properties and the microstructure in magnesium-aluminum based alloys containing strontium needs to be understood more clearly.

Acknowledgements

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